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CALIBRATION OF KILOGRAM SUBMULTIPLES

by

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The Calibration of Sub-Multiples of The Kilogram

Introduction

The kilogram is the defined unit of mass [1] in the System International, and the mass of any other material object must be related to it in as direct and unambiguous a manner as possible. This statement summarizes the task of the field of mass metrology.

Here we shall be concerned with the decimal division of the kilogram into a set of mass pieces called WEIGHTS [2] whose nominal masses bear integral ratios to the kilogram. These nominal values will be written as integers, and are the sub-multiples of the kilogram.

Sets of weights are organized in subsets called DECADES, each of whose total mass is one tenth that of the next larger decade. The members of a decade are chosen so that the minimum number of combinations produce all integral masses in the decade's range, yet permit the maximum number of comparisons of weights or groups of weights of equal nominal mass. Such a comparison, resulting in a mass difference called a DEFLECTION is referred to as a WEIGHING. The two criteria for member choice conflict in most cases and have led, as we shall see, to a number of decade organisations.

Weighing is performed using BALANCES, which are force comparators that determine deflections on the basis of gravitational force. This force is the weight of a mass, not to be confused with the word for a mass piece.

An outline of the construction or assembly of sets of weights has been given by Benoit [3], while a discussion of the behaviour of equal-arm balances has been published by Riety [4].

Traditional Mass Metrology

We first consider the calibration of a set of weights each decade of which has a distribution of nominal masses in the series 5, 3, 2, 1, 1'. The REFERENCE WEIGHT of the decade is 10. CALIBRATION is the complete procedure used to determine the mass of each weight of a decade in terms of the known mass of the reference weight. To generate a sufficient number of weighings, the additional weight 1' is included in the decade. 1' may be the sum of the weights 0.5, 0.3 and 0.2 drawn from the next smaller decade of the set. In fact, this is usually the case.

The first step in mass calibration is to establish the number of ways in which the members of a decade may be compared with one another and with the reference weight 10. The following weighings are all those possible using the chosen decade as an example:

$$
\begin{array}{cccccccc}
-10 & +5 & +3 & +2 & & & = & d_1 \\
-10 & +5 & +3 & & +1 & +1' & = & d_2 \\
-10 & +5 & +3 & +2 & +1 & -1' & = & d_3 \\
-10 & +5 & +3 & +2 & -1 & +1' & = & d_4 \\
 & +5 & -3 & -2 & +1 & -1' & = & d_5 \\
 & +5 & -3 & -2 & -1 & +1' & = & d_6 \\
 & +5 & -3 & -2 & & & = & d_7 \\
 & +5 & -3 & & -1 & -1' & = & d_8 \\
 & & +3 & -2 & -1 & & = & d_9 \\
 & & +3 & -2 & & -1' & = & d_{10} \\
 & & & +2 & -1 & -1' & = & d_{11} \\
 & & & & +1 & -1' & = & d_{12}
\end{array}
\qquad \text{(A1)}
$$

The d_i are the deflections. Members of a set of equations such as (A1) will be referred to by the set number and equation number in order, separated by a hyphen. (A1-6) is then the sixth equation of the above set, for example.

Traditionally, the set of equations (A1) were called the EQUATIONS OF CONDITION. Those involving the reference weight,10, are particularly important and were called the EQUATIONS OF DEFINITION.

Normally, a single equation of definition was used and acted as an equation of constraint. The remaining equations of condition were reduced to the number of unknowns, in this case 5 by taking each of the unknowns in turn, multiplying each equation by the coefficient of the unknown in that equation, and then adding the equations. The resulting equations, equal to the number of unknowns, were called the NORMAL EQUATIONS. These, along with a single equation of definition, were then solved for the mass of each weight. This was the "least squares" solution for the overdetermined set.

The treatment of uncertainties or the variances associated with each calibrated weight was difficult and uncertain since the statistics used with the equations of definition were different from that of the normal equations. A complete description of the traditional least squares approach will be found in [3].

A: Matrix Representation of Calibration Procedure

The treatment outlined above was state-of-the-art until the 1970s. In the last ten years, a number of authors have considered the use of least squares analysis, matrix mechanics and error analysis to maximize the knowledge obtainable from an initial set of weighings, such as set (A1). We shall apply these developments first to the mass series discussed above, and then to several others.

Series 5, 3, 2, 1, 1'

If the mass of a weight is defined as the sum of its nominal mass and a correction to the nominal mass, then set (A1) may be written entirely in terms of these corrections. They will each be written as a lower-case c subscripted by the nominal mass to which it applies, thus c_{10}.

We first address the problem of the determination of the individual c values and later consider the calculation of the variances to be ascribed to them in section C.

At the outset, a minor modification to equations (A1) is made. The correction belonging to the reference weight 10 is known. We transfer this known value to the right side of the relevant equations, completely separating the unknown c values from the known deflections and c_{10}. This seemingly trivial change in fact saves a considerable amount of mathematical manipulation. (See for example reference [5].)

We now define a single column matrix to be called the CORRECTION VECTOR, whose elements are the corrections c in descending order of nominal mass:

$$C = (c_5, c_3, c_2, c_1, c_1'). \qquad (A2)$$

These are the unknown values to be determined. We also define a single column matrix, the DEFLECTION VECTOR, whose elements are the known quantities, c_{10} and the d values, on the right side of set (A1):

$$D = (d_1 + c_{10},\ d_2 + c_{10},\ d_3 + c_{10},\ d_4 + c_{10},\ d_5 \text{ —— } d_{12}). \qquad (A3)$$

To complete the conversion of set (A1) to a useable matrix format, we define the DESIGN MATRIX, A, with elements a_{ij} to multiply a correction vector C to yield a set such as (A1). The elements of A are +1 or −1, depending on the signs ascribed to the corrections by set (A1), or 0 if the particular weight is not used. We then have the matrix equation

$$AC = D, \qquad (A4)$$

which is shown below explicitly.

$$\begin{array}{ccccc} 5 & 3 & 2 & 1 & 1' \end{array}$$

$$\begin{vmatrix} 1 & 1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 1 & 1 \\ 1 & 1 & 1 & 1 & -1 \\ 1 & 1 & 1 & -1 & 1 \\ 1 & -1 & -1 & 1 & -1 \\ 1 & -1 & -1 & -1 & 1 \\ 1 & -1 & -1 & 0 & 0 \\ 1 & -1 & 0 & -1 & -1 \\ 0 & 1 & -1 & -1 & 0 \\ 0 & 1 & -1 & 0 & -1 \\ 0 & 0 & 1 & -1 & -1 \\ 0 & 0 & 0 & 1 & -1 \end{vmatrix} \begin{vmatrix} c_5 \\ c_3 \\ c_2 \\ c_1 \\ c_{1'} \end{vmatrix} = \begin{vmatrix} d_1 + c_{10} \\ d_2 + c_{10} \\ d_3 + c_{10} \\ d_4 + c_{10} \\ d_5 \\ d_6 \\ d_7 \\ d_8 \\ d_9 \\ d_{10} \\ d_{11} \\ d_{12} \end{vmatrix} \qquad (A5)$$

Both sides of equations (A4) and (A5) may be multiplied from the left by the transpose of A, A^T. We then have, from (A4),

$$A^T AC = A^T D. \qquad (A6)$$

Equation (A6) is identical to the complete set of normal equations mentioned earlier, which include the equations of definition in the set of equations of condition. In this case, the equations of definition are not constraints on the set.

For ease of notation and because of its importance in what follows, we let

$$T = A^T A. \tag{A7}$$

T is formed by the usual rules of matrix multiplication, and is a symmetrical square matrix. This being so, T has an inverse T^{-1} such that

$$T^{-1}T = I, \tag{A8}$$

where I is the identity matrix, whose elements on the main diagonal are equal to unity and off-diagonal elements are equal to zero. Multiplying equation (A6) from the left by T^{-1} then yields:

$$C = T^{-1}A^T D \tag{A9}$$

Equation (A9) gives the least squares solution of the set of equations (A1) in matrix form. Any matrix A^T follows from any set of equations of condition and it remains only to determine T^{-1}. This presents no problem in theory, but it can be a very laborious process, unless the matrix T can be made diagonal, that is, if $t_{ij} = 0$ if $i \neq j$. Then the diagonal elements of T^{-1} are just the reciprocals of those of T.

Diagonalization of T implies that the column vectors of A are mutually orthogonal. It has been demonstrated by Grabe [6] that this condition optimizes the transfer of information inherent in the experimental data to the correction vector, C. In addition, the determination of the uncertainties or variances to be assigned to each c is made easier by choosing an ORTHOGONAL design matrix A, that is, one such that the product matrix T is diagonal.

Diagonalization of T

The problem of forming a diagonal T matrix by the selection of an orthogonal design matrix A has been addressed by several authors [5,6,7].

Beginning with a complete set of equations of condition (in our example, the set of equations (A1)) we wish to select those which lead to the formation of an orthogonal design matrix A. A number of selection rules have been proposed and justified which make the choice of equations of condition systematic.

1. Equations of condition may be used more than once, or omitted entirely. [6]
2. No row of the design matrix is considered distinct from another if it differs only by a constant factor. [7]
3. The reference weight must be the largest in the decade considered. [7]
4. If any pair of rows in the design matrix exists whose sum and difference are a second pair of rows, apart from a constant multiplier, the pairs are equivalent.

We define a set of FREQUENCIES f_1, f_2, f_3 ---- f_k, where k is the number of equations of condition; they are positive integers or zero and are equal to the number of times each equation is to be included in a new design matrix. Each row of the existing matrix A is multiplied by its corresponding frequency. The resulting matrix is multiplied by A^T.

The product matrix, P, is square and symmetric and has n rows and columns, where n is the number of variables, or weights to be calibrated. To form a new orthogonal design matrix, it appears to be sufficient to select frequency values which cause the off diagonal elements of P to vanish. The equations of constraint which accomplish this selection are given by:

$$0 = \sum_{i=1}^{k} a_{ij} a_{ih} f_i \qquad \text{(A10)}$$

The condition $j > h$ is imposed on (A10) to restrict the set to off diagonal elements and to avoid duplication of equations due to the symmetry of P. The maximum number of independent constraints is therefore $\frac{1}{2} n (n-1)$, which must provide solutions for k frequencies. k is usually larger than $\frac{1}{2} n (n-1)$ so that some of the frequencies must be set equal to zero before solution of set (A10).

Rule 4 is used to identify equivalent pairs of equations of condition. The frequencies corresponding to these equations are those which may be set equal to zero a priori. The different choices of null frequencies lead in general to different orthogonal design matrices, as we shall see.

Using the design matrix of (A5), (A10) gives the following set of ten equations:

$$
\begin{aligned}
0 &= f_1 + f_2 + f_3 + f_4 - f_5 - f_6 - f_7 - f_8 \\
0 &= f_1 + f_3 + f_4 - f_5 - f_6 - f_7 \\
0 &= f_2 + f_3 - f_4 + f_5 - f_6 - f_8 \\
0 &= f_2 - f_3 + f_4 - f_5 + f_6 - f_8 \\
0 &= f_1 + f_3 + f_4 + f_5 + f_6 + f_7 - f_9 - f_{10} \\
0 &= f_2 + f_3 - f_4 - f_5 + f_6 + f_8 - f_9 \\
0 &= f_2 - f_3 + f_4 + f_5 - f_6 + f_8 - f_{10} \\
0 &= + f_3 - f_4 - f_5 + f_6 + f_9 - f_{11} \\
0 &= - f_3 + f_4 + f_5 - f_6 + f_{10} - f_{11} \\
0 &= f_2 - f_3 - f_4 - f_5 - f_6 + f_8 + f_{11} - f_{12}
\end{aligned}
\qquad \text{(A11)}
$$

Inspection of (A1) or (A5) reveals that:

(A5-3) + (A5-4) is equivalent to (A5-1)
(A5-3) - (A5-4) " " " (A5-12)
(A5-5) + (A5-6) " " " (A5-7)
(A5-5) - (A5-6) " " " (A5-12).

In short, the rows or equations

(A5-3) and (A5-4) are equivalent to (A5-1) and (A5-12),

(A5-5) and (A5-6) are equivalent to (A5-7) and (A5-12).

The elimination of a pair of equations is accomplished simply by setting their frequencies to zero in set (A11). Noting that (A5-12) is common to both equivalences, the following sets of frequencies may be set to zero a priori in the search for orthogonal design matrices:

$$\text{a) } f_3 = f_4 = f_5 = f_6 = 0$$
$$\text{b) } f_1 = f_7 = f_{12} = 0$$
$$\text{c) } f_3 = f_4 = f_7 = 0$$
$$\text{d) } f_1 = f_5 = f_6 = 0.$$

We now examine the consequences of the choices available to us.

a) $f_3 = f_4 = f_5 = f_6 = 0$

This choice eliminates the maximum number of equations from set (A5) and allows the solution of (A11) for the remaining frequencies. This is a matter of straightforward algebra (tedious at worst) whose end result is a set of relationships between the frequencies. The solution of (A11), when the lowest non-zero frequency is one, yields

$$\begin{gathered} f_3 = f_4 = f_5 = f_6 = 0 \text{ (a priori)} \\ f_2 = f_8 = 1 \\ f_1 = f_7 = f_9 = f_{10} = f_{11} = 2 \\ f_{12} = 4 \\ \text{Total Weighings} = 16 \end{gathered} \qquad \text{(A12)}$$

Equation (A5), using the new design matrix and deflection vector resulting from using the frequencies of (A12) becomes

$$
\begin{array}{c}
\begin{matrix} 5 & 3 & 2 & 1 & 1' \end{matrix} \\
\begin{vmatrix}
1 & 1 & 1 & 0 & 0 \\
1 & 1 & 1 & 0 & 0 \\
1 & 1 & 0 & 1 & 1 \\
1 & -1 & -1 & 0 & 0 \\
1 & -1 & -1 & 0 & 0 \\
1 & -1 & 0 & -1 & -1 \\
0 & 1 & -1 & -1 & 0 \\
0 & 1 & -1 & -1 & 0 \\
0 & 1 & -1 & 0 & -1 \\
0 & 1 & -1 & 0 & -1 \\
0 & 0 & 1 & -1 & -1 \\
0 & 0 & 1 & -1 & -1 \\
0 & 0 & 0 & 1 & -1 \\
0 & 0 & 0 & 1 & -1 \\
0 & 0 & 0 & 1 & -1 \\
0 & 0 & 0 & 1 & -1
\end{vmatrix}
\end{array}
\quad
\begin{vmatrix} c_5 \\ c_3 \\ c_2 \\ c_1 \\ c_1' \end{vmatrix}
=
\begin{vmatrix}
d_1 & + c_{10} \\
(d_1)' & + c_{10} \\
d_2 & + c_{10} \\
d_7 \\
(d_7)' \\
d_8 \\
d_9 \\
(d_9)' \\
d_{10} \\
(d_{10})' \\
d_{11} \\
(d_{11})' \\
d_{12} \\
(d_{12})' \\
(d_{12})'' \\
(d_{12})'''
\end{vmatrix}
\qquad \text{(A13)}
$$

Deflections obtained by repetition of an operation are distinguished among themselves by primes. Subscripts in the deflection vectors refer to the original equations of condition (A1).

The matrices A, C and D are set out in (A13) and from them we derive T, T^{-1} and the product A^TD.

$$
T = A^TA = \begin{vmatrix}
6 & 0 & 0 & 0 & 0 \\
0 & 10 & 0 & 0 & 0 \\
0 & 0 & 10 & 0 & 0 \\
0 & 0 & 0 & 10 & 0 \\
0 & 0 & 0 & 0 & 10
\end{vmatrix} \qquad \text{(A14)}
$$

T is diagonal as required and its inverse is the matrix whose diagonal elements are the reciprocals of the diagonal elements of T:

$$
T^{-1} = \begin{vmatrix}
\frac{1}{6} & 0 & 0 & 0 & 0 \\
0 & \frac{1}{10} & 0 & 0 & 0 \\
0 & 0 & \frac{1}{10} & 0 & 0 \\
0 & 0 & 0 & \frac{1}{10} & 0 \\
0 & 0 & 0 & 0 & \frac{1}{10}
\end{vmatrix} \qquad \text{(A15)}
$$

$$A^T D = \begin{vmatrix} 3c_{10} + \sum^2 d_1 + d_2 + \sum^2 d_7 + d_8 \\ 3c_{10} + \sum^2 d_1 + d_2 - \sum^2 d_7 - d_8 + \sum^2 d_9 + \sum^2 d_{10} \\ 2c_{10} + \sum^2 d_1 - \sum^2 d_7 - \sum^2 d_9 - \sum^2 d_{10} + \sum^2 d_{11} \\ c_{10} + d_2 - d_8 - \sum^2 d_9 - \sum^2 d_{11} + \sum^4 d_{12} \\ c_{10} + d_2 - d_8 - \sum^2 d_{10} - \sum^2 d_{11} - \sum^4 d_{12} \end{vmatrix} = \begin{vmatrix} 3c_{10} + S_5 \\ 3c_{10} + S_3 \\ 2c_{10} + S_2 \\ c_{10} + S_1 \\ c_{10} + S_1' \end{vmatrix} \qquad \text{(A16)}$$

The sums S are defined by (A16).

The sigma notation used in (A16) represents the sum of deflections obtained using the same equation of condition, that is, those with the same subscript.

Finally, (A9) leads directly to the required set of calibration equations, using (A15) and (A16):

$$\begin{aligned} c_5 &= \tfrac{1}{2} c_{10} + \tfrac{1}{6} S_5 \\ c_3 &= \tfrac{3}{10} c_{10} + \tfrac{1}{10} S_3 \\ c_2 &= \tfrac{2}{10} c_{10} + \tfrac{1}{10} S_2 \\ c_1 &= \tfrac{1}{10} c_{10} + \tfrac{1}{10} S_1 \\ c_1' &= \tfrac{1}{10} c_{10} + \tfrac{1}{10} S_1' \end{aligned} \qquad \text{(A17)}$$

Note that the coefficients of the first terms in (A17) are the ratios of the nominal masses of the decade weights to the reference weight. The coefficients of the second terms are the reciprocals of the total number of times the particular weights are compared with other weights. The sums, S, contain just this number of terms.

b) $f_1 = f_7 = f_{12} = 0$

This choice leads to the following relations among the frequencies, when the lowest non-zero frequency is one:

$$\begin{gathered} f_1 = f_7 = f_{12} = 0 \text{ (a priori)} \\ f_2 = f_3 = f_4 = f_5 = f_6 = f_8 = 1 \\ f_9 = f_{10} = f_{11} = 2 \\ \text{Total Weighings} = 12 \end{gathered} \tag{A18}$$

With the aid of these frequencies the new design matrix and deflection vector are given by

$$\begin{array}{ccccc} 5 & 3 & 2 & 1 & 1' \end{array}$$

$$\begin{vmatrix} 1 & 1 & 0 & 1 & 1 \\ 1 & 1 & 1 & 1 & -1 \\ 1 & 1 & 1 & -1 & 1 \\ 1 & -1 & -1 & 1 & -1 \\ 1 & -1 & -1 & -1 & 1 \\ 1 & -1 & 0 & -1 & -1 \\ 0 & 1 & -1 & -1 & 0 \\ 0 & 1 & -1 & -1 & 0 \\ 0 & 1 & -1 & 0 & -1 \\ 0 & 1 & -1 & 0 & -1 \\ 0 & 0 & 1 & -1 & -1 \\ 0 & 0 & 1 & -1 & -1 \end{vmatrix} \begin{vmatrix} c_5 \\ c_3 \\ c_2 \\ c_1 \\ c_1' \end{vmatrix} = \begin{vmatrix} d_2 + c_{10} \\ d_3 + c_{10} \\ d_4 + c_{10} \\ d_5 \\ d_6 \\ d_8 \\ d_9 \\ (d_9)' \\ d_{10} \\ (d_{10})' \\ d_{11} \\ (d_{11})' \end{vmatrix} \tag{A19}$$

T^{-1} is identical to that given by equation (A15), and

$$A^T D = \begin{vmatrix} 3c_{10} + d_2 + d_3 + d_4 + d_5 + d_6 + d_8 \\ 3c_{10} + d_2 + d_3 + d_4 - d_5 - d_6 - d_8 + \sum^2 d_9 + \sum^2 d_{10} \\ 2c_{10} + d_3 + d_4 - d_5 - d_6 - \sum^2 d_9 - \sum^2 d_{10} + \sum^2 d_{11} \\ c_{10} + d_2 + d_3 - d_4 + d_5 - d_6 - d_8 - \sum^2 d_9 - \sum^2 d_{11} \\ c_{10} + d_2 - d_3 + d_4 - d_5 + d_6 - d_8 - \sum^2 d_{10} - \sum^2 d_{11} \end{vmatrix} = \begin{vmatrix} 3c_{10} + S_5 \\ 3c_{10} + S_3 \\ 2c_{10} + S_2 \\ c_{10} + S_1 \\ c_{10} + S_1' \end{vmatrix} \tag{A20}$$

Finally, using equations (A15) and (A20) in (A9), we arrive at a set of calibration equations which have the form of set (A17) except that the sums S are defined by equation (A20). This is the procedure first suggested by Grabe [6].

c) $f_3 = f_4 = f_7 = 0$

With this choice, the solution of set (A11) when the lowest non-zero frequency is one yields

$$f_3 = f_4 = f_7 = 0 \text{ (a priori)}$$
$$f_2 = f_5 = f_6 = f_8 = 1 \qquad \text{(A21)}$$
$$f_1 = f_9 = f_{10} = f_{11} = f_{12} = 2$$
$$\text{Total Weighings} = 14$$

The set (A21) is used to form a new orthogonal design matrix and deflection vector:

$$\begin{array}{ccccc} 5 & 3 & 2 & 1 & 1' \end{array}$$

$$\begin{vmatrix} 1 & 1 & 1 & 0 & 0 \\ 1 & 1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 1 & 1 \\ 1 & -1 & -1 & 1 & -1 \\ 1 & -1 & -1 & -1 & 1 \\ 1 & -1 & 0 & -1 & -1 \\ 0 & 1 & -1 & -1 & 0 \\ 0 & 1 & -1 & -1 & 0 \\ 0 & 1 & -1 & 0 & -1 \\ 0 & 1 & -1 & 0 & -1 \\ 0 & 0 & 1 & -1 & -1 \\ 0 & 0 & 1 & -1 & -1 \\ 0 & 0 & 0 & 1 & -1 \\ 0 & 0 & 0 & 1 & -1 \end{vmatrix} \begin{vmatrix} c_5 \\ c_3 \\ c_2 \\ c_1 \\ c_1' \end{vmatrix} = \begin{vmatrix} d_1 + c_{10} \\ (d_1) + c_{10} \\ d_2 + c_{10} \\ d_5 \\ d_6 \\ d_8 \\ d_9 \\ (d_9)' \\ d_{10} \\ (d_{10})' \\ d_{11} \\ (d_{11})' \\ d_{12} \\ (d_{12})' \end{vmatrix} \qquad \text{(A22)}$$

Once again the matrix T^{-1} is given by (A15) and

$$A^T D = \begin{vmatrix} 3c_{10} + \sum^2 d_1 + d_2 + d_5 + d_6 + d_8 \\ 3c_{10} + \sum^2 d_1 + d_2 - d_5 - d_6 - d_8 + \sum^2 d_9 + \sum^2 d_{10} \\ 2c_{10} + \sum^2 d_1 - d_5 - d_6 - \sum^2 d_9 - \sum^2 d_{10} + \sum^2 d_{11} \\ c_{10} + d_2 + d_5 - d_6 - d_8 - \sum^2 d_9 - \sum^2 d_{11} + \sum^2 d_{12} \\ c_{10} + d_2 - d_5 + d_6 - d_8 - \sum^2 d_{10} - \sum^2 d_{11} - \sum^2 d_{12} \end{vmatrix} = \begin{vmatrix} 3c_{10} + S_5 \\ 3c_{10} + S_3 \\ 2c_{10} + S_2 \\ c_{10} + S_1 \\ c_{10} + S_1' \end{vmatrix} \qquad \text{(A23)}$$

Again, using (A15) and (A23) in (A9), calibration equations result which are identical in form to set (A17), where the sums S are defined above by (A23).

d) $f_1 = f_5 = f_6 = 0$

This choice of null frequencies leads to the following solution for set (A11), when the lowest non-zero frequency is one:

$$f_1 = f_5 = f_6 = 0$$
$$f_2 = f_3 = f_4 = f_8 = 1 \qquad \text{(A24)}$$
$$f_7 = f_9 = f_{10} = f_{11} = f_{12} = 2$$
$$\text{Total Weighings} = 14$$

The frequencies from (A24) are used to form a new design matrix and deflection vector:

$$\begin{array}{ccccc} 5 & 3 & 2 & 1 & 1' \end{array}$$

$$\begin{vmatrix} 1 & 1 & 0 & 1 & 1 \\ 1 & 1 & 1 & 1 & -1 \\ 1 & 1 & 1 & -1 & 1 \\ 1 & -1 & -1 & 0 & 0 \\ 1 & -1 & -1 & 0 & 0 \\ 1 & -1 & 0 & -1 & -1 \\ 0 & 1 & -1 & -1 & 0 \\ 0 & 1 & -1 & -1 & 0 \\ 0 & 1 & -1 & 0 & -1 \\ 0 & 1 & -1 & 0 & -1 \\ 0 & 0 & 1 & -1 & -1 \\ 0 & 0 & 1 & -1 & -1 \\ 0 & 0 & 0 & 1 & -1 \\ 0 & 0 & 0 & 1 & -1 \end{vmatrix} \begin{vmatrix} c_5 \\ c_3 \\ c_2 \\ c_1 \\ c_1' \end{vmatrix} = \begin{vmatrix} d_2 + c_{10} \\ d_3 + c_{10} \\ d_4 + c_{10} \\ (d_5)' \\ (d_6)' \\ (d_8)' \\ (d_9)' \\ (d_{10})' \\ (d_{11})' \\ (d_{12})' \end{vmatrix} \qquad \text{(A25)}$$

The T^{-1} matrix is again the same as that of (A15), and

$$A^T D = \begin{vmatrix} 3c_{10} + d_2 + d_3 + d_4 + \sum^2 d_7 + d_8 \\ 3c_{10} + d_2 + d_3 + d_4 - \sum^2 d_7 - d_8 + \sum^2 d_9 + \sum^2 d_{10} \\ 2c_{10} + d_3 + d_4 - \sum^2 d_7 - \sum^2 d_9 - \sum^2 d_{10} + \sum^2 d_{11} \\ c_{10} + d_2 + d_3 - d_4 - d_8 - \sum^2 d_9 - \sum^2 d_{11} + \sum^2 d_{12} \\ c_{10} + d_2 - d_3 + d_4 - d_8 - \sum^2 d_{10} - \sum^2 d_{11} - \sum^2 d_{12} \end{vmatrix} = \begin{vmatrix} 3c_{10} + S_5 \\ 3c_{10} + S_3 \\ 2c_{10} + S_2 \\ c_{10} + S_1 \\ c_{10} + S_1' \end{vmatrix} \qquad \text{(A26)}$$

Using T^{-1} and (A26) in (A9) the calibration equations (A17) result, where the sums S are defined by (A26).

Summary: Series 5, 3, 2, 1, 1'

Using this decade organization, four methods have been found for the selection and repetition of the weighings listed in (A1) so as to produce an orthogonal design matrix. The frequencies of use of these equations are listed in Table A1.

TABLE A1

Equation	Frequency	Design Matrix a	b	c	d
(1-1)	f_1	2	0	2	0
(1-2)	f_2	1	1	1	1
(1-3)	f_3	0	1	0	1
(1-4)	f_4	0	1	0	1
(1-5)	f_5	0	1	1	0
(1-6)	f_6	0	1	1	0
(1-7)	f_7	2	0	0	2
(1-8)	f_8	1	1	1	1
(1-9)	f_9	2	2	2	2
(1-10)	f_{10}	2	2	2	2
(1-11)	f_{11}	2	2	2	2
(1-12)	f_{12}	4	0	2	2
distinct comparisons		8	9	9	9
total weighings		16	12	14	14

The matrix developed under b) involves the fewest operations and the least time and effort of the four even though the number of distinct weighings is not the minimum. It also eliminates the comparison of the nominal masses 1 and 1' which is an advantage to a balance operator. b) is the method of choice.

The four choices considered for this series resulted from the elimination of one pair of equations of condition from each equivalence. If only a single pair is eliminated a priori, then the two conditions, that there must be at least one equation of definition and that all frequencies must be zero or a positive integer, lead to one of the four choices used above.

This result has been found in the analysis of a number of weight series and suggests a corollary to rule 4: When equivalent pairs of equations are found, one pair of each equivalence should be eliminated. This procedure has been found to be a most useful starting point.

Series 5, 2, 2', 1, 1'

For a decade of this structure, 1' may be drawn from the next lower decade or from outside the set. The reference mass is 10.

First we list the weighings possible among the members of the decade and the reference weight. It is not necessary to write out a system such as (A1), since the same information is conveyed more compactly in matrix form as in (A5).

$$\begin{array}{ccccc} 5 & 2 & 2' & 1 & 1' \\ \left|\begin{array}{ccccc} 1 & 1 & 1 & 1 & 0 \\ 1 & 1 & 1 & 0 & 1 \\ 1 & -1 & -1 & -1 & 0 \\ 1 & -1 & -1 & 0 & -1 \\ 0 & 1 & -1 & 1 & -1 \\ 0 & 1 & -1 & -1 & 1 \\ 0 & 1 & 0 & -1 & -1 \\ 0 & 0 & 1 & -1 & -1 \\ 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 \end{array}\right| & \left|\begin{array}{c} c_5 \\ c_2 \\ c_2' \\ c_1 \\ c_1' \end{array}\right| & = & \left|\begin{array}{c} d_1 + c_{10} \\ d_2 + c_{10} \\ d_3 \\ d_4 \\ d_5 \\ d_6 \\ d_7 \\ d_8 \\ d_9 \\ d_{10} \end{array}\right| \end{array} \qquad \text{(A27)}$$

The design matrix, the correction vector and the deflection vector are defined by (A27) for all possible weighings.

Inspection of the design matrix indicates that the row pair (A27-5) and (A27-6) are equivalent to the pair (A27-9) and (A27-10) under rule 4. The set of frequency equations, representing the off diagonal elements of the P matrix are, from equation (A10):

$$\begin{array}{l} 0 = f_1 + f_2 - f_3 - f_4 \\ 0 = f_1 + f_2 - f_3 - f_4 \\ 0 = f_1 - f_3 \\ 0 = f_2 - f_4 \\ 0 = f_1 + f_2 + f_3 + f_4 - f_5 - f_6 - f_9 \\ 0 = f_1 + f_3 + f_5 - f_6 - f_7 \\ 0 = f_2 + f_4 - f_5 + f_6 - f_7 \\ 0 = f_1 + f_3 - f_5 + f_6 - f_8 \\ 0 = f_2 + f_4 + f_5 - f_6 - f_8 \\ 0 = - f_5 - f_6 + f_7 + f_8 - f_{10} \end{array} \qquad \text{(A28)}$$

Note that (A28-1) and (A28-2) are identical so that we have 9 equations in 10 unknowns. We now seek to generate orthogonal design matrices by setting $f_5 = f_6 = 0$ and $f_9 = f_{10} = 0$ a priori.

a) $f_5 = f_6 = 0$

The solution of set (A28) using this choice when the lowest non-zero frequency is one is:

$$\begin{array}{l} f_5 = f_6 = 0 \text{ (a priori)} \\ f_1 = f_2 = f_3 = f_4 = 1 \\ f_7 = f_8 = 2 \\ f_9 = f_{10} = 4 \end{array} \qquad \text{(A29)}$$

Total weighings = 16

b) $f_9 = f_{10} = 0$

With this choice, (A28) gives:

$$\begin{array}{l} f_9 = f_{10} = 0 \\ f_1 = f_2 = f_3 = f_4 = 1 \\ f_5 = f_6 = f_7 = f_8 = 2 \end{array} \qquad \text{(A30)}$$

Total weighings = 12

c) No frequencies set to zero a priori

Since set (A28) has only one more unknowns than equations, it reduces to the following set:

$$\begin{array}{r} 2f_1 = 2f_2 = 2f_3 = 2f_4 = f_7 = f_8 \\ f_5 = f_6 \\ f_9 = f_{10} \\ f_9 + 2f_5 = 4f_1 \end{array} \qquad \text{(A31)}$$

(A31-4) is clearly the equation of interest, and we seek sets of positive integers or zeros which satisfy it. The solution $f_1 = 0$, is both trivial and useless. Three non-trivial solutions exist for which $f_5 = 0, 2$ or 1. The first two choices lead directly to a) and b). The last, with the lowest frequency equal to one, yields:

$$\begin{array}{l} f_1 = f_2 = f_3 = f_4 = f_5 = f_6 = 1 \\ f_7 = f_8 = f_9 = f_{10} = 2 \end{array} \qquad \text{(A32)}$$

Total Weighings = 14

The system represented by set (A32) involves all possible weighings for this series.

Any of the relations (A29), (A30) or (A32) will order the construction of an orthogonal design matrix. The method was demonstrated previously for the series 5, 3, 2, 1, 1'. To repeat the entire exercise here is unnecessary. The matrix resulting from (A30) involves the fewest operations and also eliminates the comparison of the smallest weights in the decade. This is the matrix of choice.

Using (A30) we construct a new design matrix and deflection vector, drawing on equation (A27) for the selected rows or equations of condition.

$$\begin{array}{ccccc} 5 & 2 & 2' & 1 & 1' \\ \left|\begin{array}{ccccc} 1 & 1 & 1 & 1 & 0 \\ 1 & 1 & 1 & 0 & 1 \\ 1 & -1 & -1 & -1 & 0 \\ 1 & -1 & -1 & 0 & -1 \\ 0 & 1 & -1 & 1 & -1 \\ 0 & 1 & -1 & 1 & -1 \\ 0 & 1 & -1 & -1 & 1 \\ 0 & 1 & -1 & -1 & 1 \\ 0 & 1 & 0 & -1 & -1 \\ 0 & 1 & 0 & -1 & -1 \\ 0 & 0 & 1 & -1 & -1 \\ 0 & 0 & 1 & -1 & -1 \end{array}\right| & \left|\begin{array}{c} c_5 \\ c_2 \\ c_2' \\ c_1 \\ c_1' \end{array}\right| & = & \left|\begin{array}{l} d_1 + c_{10} \\ d_2 + c_{10} \\ d_3 \\ d_4 \\ d_5 \\ (d_5)' \\ d_6 \\ (d_6)' \\ d_7 \\ (d_7)' \\ d_8 \\ (d_8)' \end{array}\right| \end{array} \qquad \text{(A33)}$$

From (A33) the matrix T^{-1} is given by

$$T^{-1} = \begin{vmatrix} \frac{1}{4} & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{10} & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{10} & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{10} & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{10} \end{vmatrix} \qquad \text{(A34)}$$

and the column matrix $A^T D$ is given by

$$A^T D = \begin{vmatrix} 2c_{10} + d_1 + d_2 + d_3 + d_4 \\ 2c_{10} + d_1 + d_2 - d_3 - d_4 + \sum_2 d_5 + \sum_2 d_6 + \sum_2 d_7 \\ 2c_{10} + d_1 + d_2 - d_3 - d_4 - \sum_2 d_5 - \sum_2 d_6 + \sum_2 d_8 \\ c_{10} + d_1 - d_3 + \sum_2 d_5 - \sum_2 d_6 - \sum_2 d_7 - \sum_2 d_8 \\ c_{10} + d_2 - d_4 - \sum_2 d_5 + \sum_2 d_6 - \sum_2 d_7 - \sum_2 d_8 \end{vmatrix} = \begin{vmatrix} 2c_{10} + S_5 \\ 2c_{10} + S_2 \\ 2c_{10} + S_2' \\ c_{10} + S_1 \\ c_{10} + S_1' \end{vmatrix} \qquad \text{(A35)}$$

From equation (A9), using (A34) and (A35) we derive the final set of calibration equations.

$$c_5 = \frac{1}{2} c_{10} + \frac{1}{4} S_5$$

$$c_2 = \frac{2}{10} c_{10} + \frac{1}{10} S_2$$

$$c_2' = \frac{2}{10} c_{10} + \frac{1}{10} S_2' \qquad \text{(A36)}$$

$$c_1 = \frac{1}{10} c_{10} + \frac{1}{10} S_1$$

$$c_1' = \frac{1}{10} c_{10} + \frac{1}{10} S_1'$$

The sums S are defined by equation (A35). This design matrix in particular has been investigated in detail by Riety [5].

Series 5, 2, 1, 1', 1''

The procedure to be followed in setting up orthogonal design matrices and selecting one from among them has been covered in the analyses of the series 5, 3, 2, 1, 1' and 5, 2, 2', 1, 1'. From this point on, only the unique aspects of the analysis of any decade will be presented and repetitive comments and explanations will be omitted.

For all possible weight combinations:

$$\begin{array}{ccccc} 5 & 2 & 1 & 1' & 1'' \end{array}$$

$$\begin{vmatrix} 1 & 1 & 1 & 1 & 1 \\ 1 & -1 & -1 & -1 & -1 \\ 0 & 1 & -1 & -1 & 0 \\ 0 & 1 & -1 & 0 & -1 \\ 0 & 1 & 0 & -1 & -1 \\ 0 & 0 & 1 & -1 & 0 \\ 0 & 0 & 1 & 0 & -1 \\ 0 & 0 & 0 & 1 & -1 \end{vmatrix} \begin{vmatrix} c_5 \\ c_2 \\ c_1 \\ c_1' \\ c_1'' \end{vmatrix} = \begin{vmatrix} d_1 + c_{10} \\ d_2 \\ d_3 \\ d_4 \\ d_5 \\ d_6 \\ d_7 \\ d_8 \end{vmatrix} \qquad \text{(A37)}$$

There is only one equation of definition and no equivalences exist.

Equation (A10) yields the following:

$$\begin{aligned} 0 &= f_1 - f_2 \quad \text{(four equations identical)} \\ 0 &= f_1 + f_2 - f_3 - f_4 \\ 0 &= f_1 + f_2 - f_3 - f_5 \\ 0 &= f_1 + f_2 - f_4 - f_5 \\ 0 &= f_1 + f_2 + f_3 - f_6 \\ 0 &= f_1 + f_2 + f_4 - f_7 \\ 0 &= f_1 + f_2 + f_5 - f_8 \end{aligned} \qquad \text{(A38)}$$

The set (A38) quickly gives the relationships

$$f_1 = f_2 = f_3 = f_4 = f_5 = 1 \qquad \text{(A39)}$$

$$f_6 = f_7 = f_8 = 3$$

Total Weighings = 14

The set (A39) defines the only orthogonal design matrix. None of the rows in (A37) are eliminated but three are repeated three times. From (A39) and (A37),

$$\begin{array}{c} 5 \quad 2 \quad 1 \quad 1' \quad 1'' \\ \left|\begin{array}{ccccc} 1 & 1 & 1 & 1 & 1 \\ 1 & -1 & -1 & -1 & -1 \\ 0 & 1 & -1 & -1 & 0 \\ 0 & 1 & -1 & 0 & -1 \\ 0 & 1 & 0 & -1 & -1 \\ 0 & 0 & 1 & -1 & 0 \\ 0 & 0 & 1 & -1 & 0 \\ 0 & 0 & 1 & -1 & 0 \\ 0 & 0 & 1 & 0 & -1 \\ 0 & 0 & 1 & 0 & -1 \\ 0 & 0 & 1 & 0 & -1 \\ 0 & 0 & 0 & 1 & -1 \\ 0 & 0 & 0 & 1 & -1 \\ 0 & 0 & 0 & 1 & -1 \end{array}\right| \end{array} \left|\begin{array}{c} c_5 \\ c_2 \\ c_1 \\ c_1' \\ c_1'' \end{array}\right| = \left|\begin{array}{c} d_1 + c_{10} \\ d_2 \\ d_3 \\ d_4 \\ d_5 \\ d_6 \\ (d_6)' \\ (d_6)'' \\ d_7 \\ (d_7)' \\ (d_7)'' \\ d_8 \\ (d_8)' \\ (d_8)'' \end{array}\right| \qquad \text{(A40)}$$

from(40),

$$T^{-1} = \left|\begin{array}{ccccc} \frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{5} & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{10} & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{10} & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{10} \end{array}\right| , \qquad \text{(A41)}$$

and

$$A^T D = \left|\begin{array}{c} c_{10} + d_1 + d_2 \\ c_{10} + d_1 - d_2 + d_3 + d_4 + d_5 \\ c_{10} + d_1 - d_2 - d_3 - d_4 + \sum_3 d_6 + \sum_3 d_7 \\ c_{10} + d_1 - d_2 - d_3 - d_5 + \sum_3 d_6 + \sum_3 d_8 \\ c_{10} + d_1 - d_2 - d_4 - d_5 - \sum_3 d_7 - \sum_3 d_8 \end{array}\right| = \left|\begin{array}{c} 2c_{10} + S_5 \\ 2c_{10} + S_2 \\ 2c_{10} + S_1' \\ c_{10} + S_1' \\ c_{10} + S_1'' \end{array}\right| \qquad \text{(A42)}$$

The calibration equations, using (A41) and (A42) in (A9) are

$$c_5 = \frac{1}{2} c_{10} + \frac{1}{2} s_5$$

$$c_1 = \frac{1}{5} c_{10} + \frac{1}{5} s_2$$

$$c_1 = \frac{1}{10} c_{10} + \frac{1}{10} s_1 \qquad \text{(A43)}$$

$$c_1' = \frac{1}{10} c_{10} + \frac{1}{10} s_1'$$

$$c_1'' = \frac{1}{10} c_{10} + \frac{1}{10} s_1''$$

Calibration of the 5, 2, 1, 1', 1'', series requires the use of all possible weight comparisons. Nine of fourteen operations involve the smallest masses in the decade. In addition, if the weight 1'' is drawn from outside the decade, the members of the decade do not sum to 10. Only one equation of definition is possible in any case.

The series 5, 2, 1, 1', 1'' is not judged to be particularly desirable.

LONG mass series

The three series so far analyzed in detail have often been termed short series. Since metrologists have long felt that it is important to maximize the number of ways in which the members of a decade may be combined, to improve statistics, [3, 8] the smallest weight was divided into two equal weights to form a LONG series. An example of such a series will be analyzed for comparison with the equivalent short series.

Series 50, 20, 10, 10', 5, 5'

This is the long version of the 5, 2, 1, 1',1'' already analyzed, and the nominal masses have been multiplied by 10 so that integers may be used. The reference nominal mass is 100.

For all possible weight combinations:

$$\begin{array}{cccccc} 50 & 20 & 10 & 10' & 5 & 5' \end{array}$$

$$\begin{vmatrix} 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & -1 & -1 & -1 & -1 & -1 \\ 0 & 1 & -1 & -1 & 0 & 0 \\ 0 & 1 & -1 & 0 & -1 & -1 \\ 0 & 1 & 0 & -1 & -1 & -1 \\ 0 & 1 & -1 & -1 & 1 & -1 \\ 0 & 1 & -1 & -1 & -1 & 1 \\ 0 & 0 & 1 & -1 & 1 & -1 \\ 0 & 0 & 1 & -1 & -1 & 1 \\ 0 & 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 & -1 & -1 \\ 0 & 0 & 0 & 1 & -1 & -1 \\ 0 & 0 & 0 & 0 & 1 & -1 \end{vmatrix} \begin{vmatrix} c_{50} \\ c_{20} \\ c_{10} \\ c_{10'} \\ c_{5} \\ c_{5'} \end{vmatrix} = \begin{vmatrix} d_1 + c_{100} \\ d_2 \\ d_3 \\ d_4 \\ d_5 \\ d_6 \\ d_7 \\ d_8 \\ d_9 \\ d_{10} \\ d_{11} \\ d_{12} \\ d_{13} \end{vmatrix} \qquad \text{(A44)}$$

The pair of weights 5 and 5' are used as if they were a single piece in rows (A44-1) through (A44-5) and (A44-10) through (A44-12). These equations are equivalent to those shown in (A37). The series 5, 2, 1, 1', 1'' is a subset of (A44). The remainder of (A44) merely involve the interchange or comparison of 5 and 5'. Not surprisingly application of rule 4 yields the following equivalences:

(A44-6) and (A44-7) are equivalent to (A44-3) and (A44-13) (A45)

(A44-8) and (A44-9) are equivalent to (A44-10) and (A44-13)

Equation (A10) yields the following set of equations for the frequencies of usage of the rows of (A44):

$$0 = f_1 - f_2 \quad \text{[six equations are identical to this one]}$$

$$0 = f_1 + f_2 - f_3 - f_4 - f_6 - f_7$$

$$0 = f_1 + f_2 - f_3 - f_5 - f_6 - f_7$$

$$0 = f_1 + f_2 - f_4 - f_5 + f_6 - f_7$$

$$0 = f_1 + f_2 - f_4 - f_5 - f_6 + f_7$$

$$0 = f_1 + f_2 + f_3 + f_6 + f_7 - f_8 - f_9 - f_{10} \qquad \text{(A46)}$$

$$0 = f_1 + f_2 + f_4 - f_6 + f_7 + f_8 - f_9 - f_{11}$$

$$0 = f_1 + f_2 + f_4 + f_6 - f_7 - f_8 + f_9 - f_{11}$$

$$0 = f_1 + f_2 + f_5 - f_6 + f_7 - f_8 + f_9 - f_{12}$$

$$0 = f_1 + f_2 + f_5 + f_6 - f_7 + f_8 - f_9 - f_{12}$$

$$0 = f_1 + f_2 + f_4 + f_5 - f_6 - f_7 - f_8 - f_9 + f_{11} + f_{12} - f_{13}$$

Thus we have 11 equations in 13 unknowns, and some equations must be eliminated. Since (A44-1) is the only equation of definition, f_1 must be non-zero. Several orthogonal design matrices result from elimination of pairs of equations shown in (A45), as we have seen, for example, in the treatment of the 5, 3, 2, 1, 1' series.

a) $f_6 = f_7 = f_8 = f_9 = 0$

Setting these frequencies to zero leaves a subset of equations in (A44) which is equivalent to the 5, 2, 1, 1', 1'' series already analyzed, with one

additional comparison of the 5 and 5' weights. The solution of (A46) is very simple and when the smallest non-zero frequency is one, yields the relations:

$$\begin{aligned} f_6 = f_7 = f_8 = f_9 &= 0 \text{ (a priori)} \\ f_1 = f_2 = f_3 = f_4 = f_5 &= 1 \\ f_{10} = f_{11} = f_{12} &= 3 \\ f_{13} &= 10 \end{aligned} \qquad \text{(A47)}$$

Total Weighings = 24

It is left to the reader to set up the orthogonal design matrix and the new deflection vector, the T^{-1} matrix, and the product $A^T D$.

The end result of this process is a set of calibration equations which is the same as that given in (A43) with the exception of (A43-5). This equation is replaced by two equations for the weights 5 and 5':

$$c_5 = \frac{1}{20} c_{100} + \frac{1}{20} S_5$$

$$c_5' = \frac{1}{20} c_{100} + \frac{1}{20} S_5' \qquad \text{(A48)}$$

The long series has not contributed in any way to the calibration of the weights 50, 20, 10 and 10'. It is true that 5 and 5' have been calibrated, but the additional ten comparisons hardly seem worthwhile. If the next decade has the 5,2,1,1',1'' structure then all members of that decade can be calibrated in only 14 operations.

The subdivision of the last member of a short series in order to increase the number of mass comparisons would appear to be both laborious and of little value.

b) $f_3 = f_{10} = 0$

This series is one of the few in which rule 4 cannot be rigourously applied. The reader may verify that setting $f_{13} = 0$ does not allow the solution of set (A46). The solution of (A46) yields the following relations:

$$\begin{aligned} f_3 = f_{10} &= 0 \text{ (a priori)} \\ f_6 = f_7 &= 1 \\ f_1 = f_2 = f_4 = f_5 &= 2 \\ f_8 = f_9 &= 3 \\ f_{11} = f_{12} &= 6 \\ f_{13} &= 12 \\ \text{Total Weighings} &= 40 \end{aligned} \qquad \text{(A49)}$$

Further investigation of the orthogonal matrix generated by the frequencies (A49) is not productive. It would appear that the only argument which may be presented for the use of long series is the number of weighings (equations) involved. If for any reason this is felt to be a desirable feature, one need only repeat the weighings of the short series as many times as necessary.

B: Air Buoyancy Effects

In section A, some methods have been presented for generation of orthogonal design matrices for calibration of sets of weights in terms of a reference weight. The development of equations such as (A17), (A36) or (A43) takes no account of the fact that the mass comparisons are carried out in air under ambient conditions. In this section, the effects of air buoyancy will be incorporated into the calibration equations. A balance is a force comparator, and in air with density ρ_a, the weight w (force) due to gravitation acting on an object of mass m and density ρ is, using Archimedes principle,

$$w = mg\ (1 - \frac{\rho_a}{\rho}) = K\ mg, \qquad (B1)$$

where g is the local acceleration due to gravity. The factor K will be called the BUOYANCY.

We consider a weighing carried out using a single pan balance or an equal arm balance in substitution mode. Weighings are performed with the aid of a SENSITIVITY WEIGHT of known total mass δ and density ρ_s in the following manner, to obtain the mass of an object, m.

The object is placed on the balance pan and produces a balance indication or reading r, which is related to the mass of the object by

$$Km = \beta r. \qquad (B2)$$

β is the balance CALIBRATION FACTOR, a constant of proportionality which is the reciprocal of the balance SENSITIVITY. The sensitivity weight δ is added to the balance pan, producing a second balance reading r_s, so that

$$Km + K_s\delta = \beta r_s \qquad (B3)$$

Equation (B2) and (B3) are combined to eliminate β, and result in an equation which relates the mass of the object to known values and parameters:

$$Km = K_s \delta \left(\frac{r}{r_s - r}\right). \tag{B4}$$

We define the EFFECTIVE MASS of an object as the product of its mass and buoyancy. The difference in the effective masses of two nominally equal groups of weights is the deflection defined earlier. A single comparison of n weights divided into two groups of nominally equal mass takes the form

$$\sum_{i=1}^{n} \pm K_i m_i = K_s \, \delta \left[\frac{r}{r_s - r} - \frac{r'}{r_s' - r'}\right] \tag{B5}$$

where the signs on the left side determine to which group a particular mass belongs, and primes distinguish the balance readings obtained for the two groups. The sign assignment is immaterial provided that it is consistent. Any deflection in observed mass units (for $K_s = 1$) is given by

$$d = \delta \left[\frac{r}{r_s - r} - \frac{r'}{r'_s - r'}\right] = \delta A \ . \tag{B6}$$

The exact form of A may vary with the comparison procedure chosen - the balance type and its operation, or the handling of balance data. It will always, however, be a sum of dimensionless ratios of balance readings.

If for any substitution weighing the balance calibration factor is defined by

$$\beta = \frac{2\delta}{r_s + r'_s - r - r'} \ , \tag{B7}$$

then the form of any observed deflection is given by

$$d = \beta (r - r') = \delta A. \tag{B8}$$

Deflections computed from (B6) and (B8) are the same when $(r_s - r)$ is equal to $(r'_s - r')$. This equality obtains when balance sensitivity is high (β is low). When sensitivity is low experiment has shown that (B8) produces markedly lower dispersions of the residuals (discussed in Section C). (B7) and (B8) are therefore the forms chosen for use in the Mechanical Standards Laboratory. β has the same buoyancy as δ.

At the outset, the mass of an object m was defined as the sum of its nominal mass M and a correction to it, c:

$$m = M + c. \tag{B9}$$

In order to consider the effects of air buoyancy we must include the entire masses of compared objects. The subscripts u and r will be used to identify a weight to be calibrated and a reference weight respectively. It is easy to show that for any of the calibration equations, the relation between the total masses of an unknown and a reference weight is given by

$$m_u = \alpha m_r + \frac{1}{n} S, \tag{B10}$$

where α is the ratio of the nominal masses

$$\alpha = M_u / M_r \tag{B11}$$

and n is an integer equal to the number of deflections in the sum S.

The equations (B10) were developed as if the mass comparisons were performed in vacuum. In air the effective mass equation is

$$K_u m_u = \alpha K_r m_r + \frac{K_s}{n} S. \tag{B12}$$

Using (B9) and (B11) in (B12),

$$K_u(M_u + c_u) = \frac{M_u}{M_r} K_r (M_r + c_r) + \frac{K_s S}{n}, \tag{B13}$$

and rearranging,

$$c_u = \frac{1}{K_u} \left[M_u(K_r - K_u) + \frac{K_r M_u}{M_r} c_r + \frac{K_s S}{n} \right]. \tag{B14}$$

As the air density tends to zero, the buoyancies tend to unity and (B14) reduces to the form of the calibration equations previously derived.

If m_u, m_r and δ all have the same density, then once again the calibration equation reduces to the simple form

$$c_u = \alpha c_r + \frac{1}{n} S, \tag{B15}$$

as given in equations (A17), (A36) and (A43).

The sum S in (B14) and (B15) is a sum of signed deflections of the type given in (B6) or (B8) so that

$$S = \delta \sum_{i=1}^{n} A_i. \tag{B16}$$

C: Uncertainties in Mass Corrections

In this section the uncertainties to be ascribed to mass corrections will be calculated, using as a starting point the general equation for c_u, (B14). Since the nominal masses are defined quantities they have no uncertainties, and the ratio α (from (B11)) is reintroduced into equation (B14):

$$c_u = \frac{1}{K_u}\left[M_u(K_r - K_u) + K_r \alpha c_r + \frac{K_s S}{n}\right] \qquad (C1)$$

Using the symbol Δ to represent differentials, the relation between the total differential of c_u and the differentials of the variables on the right side of (C1) is given by

$$\Delta c_u = \frac{1}{K_u^2}\left[\alpha K_r K_u \Delta c_r + \frac{K_s K_u}{n}\Delta S + \frac{K_u S}{n}\Delta K_s\right.$$

$$\left. + (M_u + \alpha c_r)(K_u \Delta K_r - K_r \Delta K_u) - \frac{K_s S}{n}\Delta K_u\right] \qquad (C2)$$

The relative magnitudes of the terms on the right side of (C2) vary considerably and the task in hand is simplified if some of them can safely be eliminated. The following short table supplies typical information about air and materials used in the manufacture of weight sets which will be useful.

TABLE C1

Material	Symbol	Density, ρ (kg/m^3)	Buoyancy K	$1 - K$ (ρ_a/ρ)
Air	-	1.2	0	1
Aluminum	Al	2 700	0.999 556	4.4×10^{-4}
Stainless Steel	SS	7 800	0.999 846	1.5×10^{-4}
Brass	Br	8 400	0.999 857	1.4×10^{-4}
Tantalum	Ta	16 600	0.999 927	7.2×10^{-5}
90% Platinum 10% Iridium	Pt/Ir	21 500	0.999 944	5.6×10^{-5}

On the basis of the data shown in Table C1 a good approximation to the exact equation (C2) may be made by setting all buoyancies equal to unity, leaving

$$\Delta c_u = \alpha \Delta c_r + \frac{1}{n} \Delta S + \frac{S}{n} (\Delta K_s - \Delta K_u) + (M_u + \alpha c_r) (\Delta K_r - \Delta K_u). \qquad (C3)$$

Further simplification of (C3) is possible through consideration of the type or class of weights to be calibrated. Typically, sets of weights are of class S or S-1 for which tolerances or maximum values of corrections have been defined [10]. Some values for an S-1 set are given in table C2.

TABLE C2

Tolerances for S-1 Weights

Nominal Value	Tolerance (mg)	Tolerance / Nominal Mass
1 kg	10	10^{-5}
100 g	1	10^{-5}
10 g	0.25	2.5×10^{-5}
1 g	0.1	1×10^{-4}
100 mg	0.05	5×10^{-4}
10 mg	0.03	3×10^{-3}
1 mg	0.025	2.5×10^{-2}

The smallest reference weight used in set calibration is 10 mg, so that setting $c_r = 0$ in the last term in (C3) changes the term value by a maximum of 0.3%. Similarly, the maximum allowable value of S/n (when $c_r = 0$) is the total correction for a given weight. For any reasonable set of buoyancy differentials, then, the third term in (C3) may be set equal to zero. Under these approximations (C3) becomes

$$\Delta c_u = \alpha \Delta c_r + \frac{1}{n} \Delta S + M_u (\Delta K_r - \Delta K_u). \qquad (C4)$$

From equation (B1),

$$\Delta K = \frac{\rho_a \Delta\rho}{\rho^2} - \frac{\Delta\rho_a}{\rho}, \tag{C5}$$

and using this relation in the final term of (C4) yields

$$\Delta c_u = \alpha \Delta c_r + \frac{\Delta S}{n} + M_u\left[\rho_a\left(\frac{\Delta\rho_r}{\rho_r^2} - \frac{\Delta\rho_u}{\rho_u^2}\right) + \Delta\rho_a\left(\frac{1}{\rho_u} - \frac{1}{\rho_r}\right)\right] \tag{C6}$$

The term in ΔS will be discussed at a later point in this development.

In order to obtain an uncertainty estimate for c_u, we now replace the differentials with the standard deviations of the variables. The only variables which may be correlated are ρ_r and ρ_u. The covariances of all other pairs of variables are taken to be equal to zero. The variance of c_u, from (C6) is

$$V(c_u) = \alpha^2\, V(c_r) + \frac{V(S)}{n^2} + M_u^2\left[V(\rho_a)\left(\frac{1}{\rho_u} - \frac{1}{\rho_r}\right)^2\right. \tag{C7}$$

$$\left. + \rho_a^2\left(\frac{V(\rho_r)}{\rho_r^4} - \frac{2\Delta\rho_r \Delta\rho_u}{\rho_r^2 \rho_u^2} + \frac{V(\rho_r)}{\rho_u^4}\right)\right]$$

The only practical situation in which the covariance $\Delta\rho_r \Delta\rho_u$ is non-zero occurs when M_u and M_r are made from the same ingot of uniform density, when $\rho_u = \rho_r$ and $\Delta\rho_r$ and $\Delta\rho_u$ are equal and correlated. Under these conditions

$$V(c_u) = \alpha^2 V(c_r) + \frac{V(S)}{n^2}. \tag{C8}$$

When no correlation exists between ρ_u and ρ_r (that is, there exists no functional relation between them) (C7) becomes

$$V(c_u) = \alpha^2 V(c_r) + \frac{V(S)}{n^2} + M_u^2\left[V(\rho_a)\left(\frac{1}{\rho_u} - \frac{1}{\rho_r}\right)^2\right. \tag{C9}$$

$$\left. + \rho_a^2\left(\frac{V(\rho_r)}{\rho_r^4} + \frac{V(\rho_u)}{\rho_u^4}\right)\right] .$$

Variance of S

The first step in assessing the value of V(S) is to determine the variance of the residuals in a decade calibration. The residuals are obtained by inserting the corrections calculated from the calibration equations in the equations of condition and definition to produce an expectation value of each of the deflections. The difference between the expectation value and the measured deflection is the residual. The sign of the difference is immaterial provided that the order of subtraction is consistent.

The group variance of the residuals is given by

$$V(R) = \frac{1}{(k-j)} \sum_{i=1}^{k} R_i^2 \qquad (C10)$$

where k is the total number of comparisons, j is the number of independent unknowns (corrections) and R_i is the residual for the i^{th} comparison. V(R) is the variance ascribed to each deflection. These deflections are a product of the mass of the sensitivity weight δ and a sum of quotients of balance readings, A as given by (B8). The value of δ is supplied ab initio and is invariant during decade calibration. We therefore have

$$V(d) = V(R) = \delta^2 V(A) \qquad (C11)$$

For any calibration equation, then, the variance of the sum S expressed in (B16) is

$$V(S) = V(\delta) \sum_{i=1}^{n} (A_i)^2 + \delta^2 \sum_{i=1}^{n} V(A_i) \qquad (C12)$$

Using (B8) and (C11) to simplify (C12) produces

$$V(S) = \frac{V(\delta)}{\delta^2} \sum_{i=1}^{n} d_i^2 + nV(R). \qquad (C13)$$

Substituting V(S) from (C13) in (C8) and (C9) we arrive at the final equations for $V(c_u)$:

When the unknown and reference weights are made from the same uniform ingot,

$$V(c_u) = \alpha^2 V(c_r) + \frac{V(R)}{n} + \frac{V(\delta)}{(\delta n)^2} \sum_{i=1}^{n} d_i^2 \qquad \text{(C14)}$$

and when these masses are uncorrelated,

$$V(c_u) = \alpha^2\ V(c_r) + \frac{V(R)}{n} + \frac{V(\delta)}{(\delta n)^2} \sum_{i=1}^{n} d_i^2 \qquad \text{(C15)}$$

$$+ M_u^2 \left[V(\rho_a) \left(\frac{1}{\rho_u} - \frac{1}{\rho_r}\right)^2 + \rho_a^2 \left(\frac{V(\rho_r)}{\rho_r^4} + \frac{V(\rho_u)}{\rho_u^4}\right)\right] .$$

The magnitude of the third term on the right of (C14) and (C15) is not immediately obvious. Only the second and third terms depend on the weighing process; the other variances are obtained from data extrinsic to the weighings.

We combine the two terms in the form

$$\frac{V(R)}{n} \left[1 + \frac{V(\delta)}{V(R)\delta^2} \frac{1}{n} \sum_{i=1}^{n} d_i^2 \right] . \qquad \text{(C16)}$$

The factor $\frac{1}{n} \sum_{i=1}^{n} d_i^2$ is the mean square deflection and is a measure of the size of the corrections in a decade. If all the weights have nominal mass this term is equal to zero. The group variance V(R) depends on the precision of the balance employed and the skill of the operator.

In order to compare the second bracketed term in (C16) with unity, approximate values of V(R) are given in table C3. These variances were obtained from the calibration of three sets of weights and are representative only. From the same calibrations, representative values of the mean square deflections are given in the same table. Similarly, for either a 1 mg or 5 mg sensitivity weight the value of $V(\delta)/\delta^2$ is taken to be 2×10^{-7}.

Finally, in the fourth column of table C3 will be found the values of the second bracketed term in (C16).

TABLE C3

DECADE	V(R) (mg^2)	$\frac{1}{n}\sum_{i=1}^{n} d_i^2$	Second Term (C16)
100 - 500 g	7.0×10^{-2}	2.0×10^{-1}	6×10^{-7}
10 - 50 g	2.5×10^{-4}	4.0×10^{-2}	3×10^{-5}
1 - 5 g	2.5×10^{-4}	9.0×10^{-3}	7×10^{-6}
100 - 500 mg	2.2×10^{-6}	5.0×10^{-3}	5×10^{-4}
10 - 50 mg	2.2×10^{-6}	2.0×10^{-3}	2×10^{-4}
1 - 5 mg	2.2×10^{-6}	2.4×10^{-3}	2×10^{-4}

It is apparent from the data of table C3 that the variance of the sensitivity weight may be ignored during calibration of weights in classes M, S, S-1 and J (see [10]). However, if the mean square deflection is very large, then the variance of the sensitivity weight may not be negligible. A set of weights for which this is true is unlikely to find its way to a national standards laboratory.

The air density ρ_a is computed by the methods outlined in [11]. The computation of $V(\rho_a)$ from the published equations is both daunting and unnecessary. The value of ρ_a depends upon atmospheric temperature, T, pressure, P, humidity, H, and carbon dioxide content. Since each parameter is independently measured in situ, they may be considered mutually uncorrelated in the open atmosphere. In the mass calibration range discussed here, the carbon dioxide content of the atmosphere may be considered constant.

Under normal laboratory conditions ρ_a varies linearly with T, P and H about a median set of values peculiar to a given laboratory and time. In terms of constants of proportionality x, y, z , we may represent the total differential of ρ_a as

$$\Delta\rho_a = x\Delta P - y\Delta T - z\Delta H \ . \qquad \text{(C16)}$$

Once again if the differentials on the right side of (C16) are taken to represent uncertainties of measurement (not necessarily the standards of deviation) then the variance of ρ_a is approximated by

$$V(\rho_a) = (x\Delta P)^2 + (y\Delta T)^2 + (z\Delta H)^2 . \qquad \text{(C17)}$$

The values of x, y and z computed from [11] were found to be

$$\begin{aligned} x &= 1.18 \times 10^{-5} \quad (kg/m^3)/Pa \\ y &= 4.15 \times 10^{-3} \quad (kg/m^3)/K \\ z &= 1.22 \times 10^{-4} \quad (kg/m^3)/\% \end{aligned} \qquad \text{(C18)}$$

As an example, suppose that the uncertainties in P, T and H over the duration of a decade measurement are $\Delta P = 300$ Pa, $\Delta T = 0.5$ K, $\Delta H = 2\%$.

Using the uncertainties and the coefficients (C18) in (C17),

$$V(\rho_a) = 1.69 \times 10^{-5} \ (kg/m^3)^2 , \qquad \text{(C19)}$$

from which

$$\Delta\rho_a = 4.11 \times 10^{-3} \ (kg/m^3), \qquad \text{(C20)}$$

In the normal course of events it may be necessary to derive $V(\rho_u)$ and $V(\rho_r)$ from relatively crude estimates of the uncertainties in the densities. The judgements to be made in these cases are complex and often subjective and will not be discussed here.

D: Bootstrapping; the Sensitivity Weight and the Final Decade.

The sensitivity weight is used in the calibration of a decade as a means of calibrating the balance. In the calculation of the variance of the residuals it is implicit that all comparisons for a given decade be performed on a single balance, using a single sensitivity weight.

Decade series type, balance and sensitivity weight may vary from decade to decade. The reference weight for any decade is a weight from the next larger decade whose nominal mass is an integral power of ten. For balances of sufficient sensitivity to perform the calibrations discussed here, the sensitivity weight will have a nominal mass of 1 to 5 mg, but in principle may be drawn from any decade lower than that being calibrated.

We now consider the origin of the calibration of sensitivity weights. Introducing them from outside a set begs the question. Our aim, then, is to completely calibrate a set of weights in a closed fashion in which the only weight external to the set is an initial reference weight - usually a reference kilogram.

a) The Final Decade

Since the final decade (usually 5 - 1 mg) by definition has no source of sensitivity weights native to the set, its calibration is tied to that of the PENULTIMATE or next-to-last decade.

We stipulate that the final and penultimate decades be calibrated using the same balance. The calibration of the balance must be constant over the dynamic range of the two decades, a nominal mass range of 1 to 100 mg for the sets discussed here. Adherence to this criterion may easily be verified.

The penultimate decade is calibrated in the normal way, using a sensitivity weight drawn from the final decade (normally 1 mg). The same balance readings are used to obtain the mean calibration factor of the balance which is then used in the calibration of the final decade.

To calibrate the final decade, only two balance readings per weighing are required - one with each of the masses to be compared. Using the mean calibration factor computed using (B7) for the penultimate decade, any deflection is given by (B8):

$$d = \beta(r-r'). \tag{D1}$$

The variance of the residuals, V(R), is obtained using (C10) and we have

$$V(d) = V(R) = \beta^2 V(r-r') \tag{D2}$$

For the calibration equations, the required sum of n deflections is

$$S = \beta \sum_{i=1}^{n} (r - r')_i , \tag{D3}$$

in analogy with (B16).

The variance of S is

$$V(S) = V(\beta) \sum_{i=1}^{n} (r-r')_i^2 + \beta^2 \sum_{i=1}^{n} V(r-r')_i . \tag{D4}$$

Using (D1) and (D2) to simplify (D4) given

$$V(S) = \frac{V(\beta)}{\beta^2} \sum_{i=1}^{n} d_i^2 + nV(R). \tag{D5}$$

Compare (D5) with (C13). The remarks on the magnitude of $V(\delta)/\delta^2$ in section C also apply to the factor $V(\beta)/\beta^2$.

In effect, β is used in place of δ and $V(\beta)$ in place of $V(\delta)$ for the final decade. It remains only to determine the form of $V(\beta)$, using the data from the penultimate decade. Let

$$\beta = \delta\gamma \tag{D6}$$

for the penultimate decade, where β and γ are mean values and γ has units of reciprocal balance readings. The variance of β is then

$$V(\beta) = \delta^2 V(\gamma) + \frac{\beta^2}{\delta^2} V(\delta). \qquad (D7)$$

Using (D6) in (D7)

$$\frac{V(\beta)}{\beta^2} = \frac{V(\gamma)}{\gamma^2} + \frac{V(\delta)}{\delta^2} . \qquad (D8)$$

Note that the first term on the right side of (D8) is $V(\beta)/\beta^2$ when $V(\delta)$ is equal to zero. This term is readily obtained from experimental data.

For the final decade, then, β replaces δ and $V(\beta)$ replaces $V(\delta)$ in (C14) and (C15). Note that $V(\beta)$ and $V(\delta)$ are <u>not</u> the variances of the means. These values would produce an artifically low value for the variance of the corrections computed for the final decade.

<u>b) The Sensitivity Weight</u>

Having established a method for calibration of the final decade without using a sensitivity weight, we have succeeded only in calibrating it in terms of one of its own members and a reference weight. The actual calibration of the sensitivity weight may be carried out in a series of successive approximations.

For the sake of clarity, we consider a complete set of weights ranging in mass from 500 g to 1 mg in six decades to be calibrated in terms of a reference kilogram. The 1 mg weight is used as the reference weight in all decades.

Ab initio, the correction to the 1 mg weight is unknown or poorly known, so that an estimate ε is used in the set calibration, and

$$\delta = 1 + \varepsilon \qquad (D9)$$

The calibration equation for the 1 mg correction, c_1, for any series analyzed in section A is

$$c_1 = \frac{1}{10} c_{10} + \frac{1}{10} S_1 \qquad (D10)$$

which may be written

$$c_1 = \frac{1}{10} c_{10} + \delta B_1 \qquad \text{(D11)}$$

where B_1 is a collection of balance readings - experimental data which may be considered as fixed.

The form of (D11) is the same for c_{10}, c_{100} — so that c_1, may be written in terms of a regressive series

$$c_1 = 10^{-6} c_{kg} + \delta(B_1 + \frac{1}{10} B_{10} + \frac{1}{100} B_{100} \text{---}) \qquad \text{(D12)}$$

Equation (D12) expresses the correction to the 1 mg weight in terms of known data and the estimate of its own value in δ. (D12) is more simply written using (D9) as

$$c_1 = \phi + \theta + \varepsilon\theta \qquad \text{(D13)}$$

so that we have the correction c_1 in terms of constants and its own estimate ε. If now c_1 from (D13) is used in place of ε, a second value or estimate of c_1 is obtained. This iteration may be repeated several times, of course, and leads to a series solution for c_1:

$$c_1 = (\phi + \theta) \sum_{i=0}^{n} \theta^i + \varepsilon\theta^{n+1} \qquad \text{(D14)}$$

Since θ is always less than unity the power series in θ converges. It is evident from (D14) that the simplest initial value for the estimate ε is zero.

For $|\theta| < 1$ the convergence limit of the geometric series is $1/(1-\theta)$ so that with $\varepsilon = 0$ (D14) becomes

$$c_1 = (\phi + \theta)/(1-\theta). \qquad \text{(D15)}$$

It is easy to generalize (D15) to apply to any sensitivity weight of nominal mass M_s:

$$c_s = (\phi + M_s\theta)/(1-\theta) \qquad \text{(D16)}$$

where

$$\phi = \frac{M_s}{1\ \text{kg}} c_{kg} \qquad \text{(D17)}$$

Thus it is possible to calibrate the sensitivity weight in a closed fashion. It is then only necessary to use the correction from (D15) to recalculate the corrections for all other members of the set. If more than one sensitivity weight is used to calibrate a set, the above procedure still applies.

In practice, the geometric series in (D14) converges very rapidly, and since it is necessary to recalculate all the corrections in a set in any case, it is usually convenient simply to reanalyze the entire set in terms of the calculated approximations to the corrections to the various sensitivity weights.

A number of experimental tests of closure have been performed. One involved the use of a 100 mg weight as a reference for the calibration of the final two decades of a weight set using the procedures discussed in this section. The reference weight was 1 mg from the last decade. Beginning with initial estimates of the total mass of the sensitivity weight and reiterating the result of each calibration produced the values for δ shown in the following table. Numbers represent masses in milligrams, for four successive calibrations.

TABLE D1

Initial	Cal 1	Cal 2	Cal 3	Cal 4
10	1.1461	1.0166	1.0147	1.0147
2	1.0291	1.0149	1.0147	1.0147
1	1.0145	1.0147	1.0147	1.0147
0.5	1.0071	1.0146	1.0147	1.0147

The closure is rapid, even when initial estimates are an order of magnitude larger than the nominal mass. Further calculations using experimental data for the calibration of entire sets using two sensitivity weights indicate that if δ is taken to be equal to the nominal mass, closure is complete after the second recalculation.

The general procedure used when more than one sensitivity weight is employed in a set calibration is simple. The first calculation of the calibration equations is carried out using the best available values for the sensitivity masses, if they exist, or their nominal masses. The second and any subsequent calculations employ the sensitivity masses from the previous calculation.

E: Summary of Procedures

In the foregoing sections the selection and construction of orthogonal design matrices has been outlined and some final calibration equations developed for three decimal weight series and for the binary pound series (Section A and Appendix A). The calculation of the effects of air buoyancy was discussed in section B, and the derivation of variances (or uncertainties) in section C. In section D methods were developed for closed calibration of a set of weights including the sensitivity weights.

We now present a stepwise guide to the calibration of a decimal set of weights with reference to specific equations and procedures contained in sections A through D. It will be assumed that each decade is organized in one of the series treated in section A: 5, 3, 2, 1, 1' or 5, 2, 2', 1, 1' or 5, 2, 1, 1',1''. If this is not the case, the user may employ the information in section A to derive his own orthogonal matrix and calibration equations.

The reference weight for the set will be one kilogram (nominal) whose correction and variance are taken as given. The set will be taken to be organized in six decades including nominal masses ranging from 500 g to 1 mg inclusive.

The series organization of each decade need not be consistent throughout the set, but consistency is convenient. Here "higher" and "lower" decades refer to those of larger and smaller nominal masses than the particular decade being discussed.

In section A several orthogonal matrices were found to be available for some series. The choice of which to use will depend on several factors which do not affect the mathematics, such as balance selection and the number of manipulations required of the operator. For convenience, the following matrices

and equations have been selected for use here. This selection represents value judgements made by the author; for details see the text. The numbers in Table E1 are equation numbers from section A.

TABLE E1

Series	Design Matrix	Calibration	Deflection Summations
5, 3, 2, 1, 1'	(A19)	(A17)	(A20)
5, 2, 2',1, 1'	(A33)	(A36)	(A35)
5, 2, 1, 1',1''	(A40)	(A43)	(A42)

a) Calibration Procedure ab initio

First Decade

Reference Weight	1 kg with given correction and variance.
Balance	one only for entire decade
Sensitivity Weight	one only for entire decade. Drawn from any lower decade, preferably the last. Total mass taken as nominal. Variance taken as zero.
Corrections	For decade series, table E1
Residuals	Use design matrix equation, table E1, and above numeric corrections to form a computed deflection vector. The difference between the computed and experimental vectors yields the group variance of residuals V(R) obtained from (C10).

No Air Buoyancy	Compute variances of corrections (C14).
	Calibration of decade is completed.
Air Buoyancy	Compute air density [11] and variance (C17) or equivalent.
	Compute corrections (B14) and variances (C15)
	Calibration of decade is completed
Second, Third, Fourth Decades	
Reference Weight	Smallest weight (integral power of 10) from next higher decade with its correction and variance.
	Proceed as for First Decade
Fifth (Penultimate) Decade	
Balance	Compute mean balance calibration factor - mean of β from (B7)
	Compute variance of β from (D7)
	Otherwise proceed as for decades 2,3,4.

Sixth (Final) Decade

Balance	The balance must be the same one used for the penultimate decade calibration.
Sensitivity Weight	Balance calibration and its variance, from penultimate decade, are used instead of sensitivity weight and its variance. Otherwise proceed as for decades 2,3,4.

b) Second and Subsequent Approximations

All necessary experimental data have been obtained in the ab initio calibration. The calculations are simply repeated using the corrections to the sensitivity weights obtained from the ab initio calibrations.

Similarly, the results of the second approximation may be used to generate a third. In general, however, it will seldom be necessary to carry out approximations beyond the second or third since closure is rapid. (see Section Db).

Discussion

This report is based on the premise that sets of weights comprising several decades complete with sensitivity weights may be calibrated ab initio in terms of a reference kilogram.

It is clear that calibration may be piecemeal, decade by decade, since each decade calibration is a complete and isolated event relating the masses of specific weights to that of a reference weight. Variances ascribed to weights by the methods of Section C are based on the assumption of normal distribution of the uncertainties cited. No account is taken of systematic uncertainties attributable, for example, to changes in a balance or its operation between calibrations.

We now assume that systematic uncertainties obtaining during specific decade calibrations are themselves normally distributed among repeated calibrations. For a single calibration, the best estimate of a correction's variance is given by (C14) or (C15). If, however, several determinations are made, they are given equal statistical weight and the best estimate of the value of a correction is taken to be the arithmetic mean of the determinations, the CUMULATIVE MEAN. The variance of this mean is computed from the group of independent values which is considered to be a sample of normally distributed values.

Each time a decade is recalibrated, new values of its members' corrections are added to their respective pools and new cumulative means and variances computed. Calibration records for each weight reveal monotonic changes associated, for example, with wear and mass loss if any. These records also monitor the measurement process and the condition of each weight.

This procedure permits the establishment of acceptance criteria. In the Mechanical Standards Laboratory, if the correction for a weight differs from the previous cumulative mean by twice the standard deviation of the mean, the weight is suspect.

After several calibrations of a set, the cumulative means of its members' corrections assume a significance which alters the set calibration procedure. The 100g weight from the first decade is the reference weight for the second. Its cumulative mean value serves as the reference value for the calibration of the second decade. The cumulative mean for the 10g weight belonging to the second decade serves as the reference for the third and so on.

This calculation is repeated for the existing calibrations of each of the lower decades in turn, to produce current "best" estimates for the corrections for all members of the set as well as their variances.

Arguments can be made to justify discarding older calibrations so that cumulative means are computed only from a fixed number of the most recent calibrations. Such a procedure may be justified, for example, if set members' corrections exhibit monotonic changes due to wear. However, the establishment of such a policy depends heavily on the experience and expectations of specific laboratories. For this reason, no judgements or recommendations will be made here.

The Sum or Closure Weight(s)

It was pointed out in Section A that the closure weight (an integral power of ten) may be drawn from the next lower decade. In fact, if only one set of weights is available, this summation option is mandatory.

When the correction to a sum closure weight is obtained, it plays no intrinsic role in the set calibration. However, its value and variance may be useful as a check on the statistical control which is maintained over the entire measurement process.

As an example, consider the previously cited set in which all decades are organized in the 5,3,2,1,1' series. For the calibration of the first decade (100 to 500 grams) the closure weight, 100', is made up of the sum 50+30+20 grams. When the second decade is calibrated in terms of the 100g weight from the first, corrections and variances are obtained for each member of the 100' sum. A comparison of 100' as measured in the first and second decade calibrations provides a measure of statistical control.

It is important to realize that during a calibration, the deflections are uncorrelated. However a correlation exists between each calibrated weight and the reference weight from the next higher decade. This correlation depends on the first terms on the right sides of (C14) and (C15). By extension, of course, the correlation between any weight and a reference kilogram is calculable and may be extended back to the reference kilograms used by the Bureau International des Poids et Mesures, in fact. It must be concluded that the covariance between the members of a sum of weights must be taken into consideration since the covariance terms are not small.

Because of this correlation among the weights of a set and between sets, in the Mechanical Standards laboratory the best estimate of the standard deviation of the correction to a sum of weights is taken to be the sum of the standard deviations of the members of the sum.

Check Weights

The action outlined above is useful when the procedures and equipment of a mass laboratory are being established. If two or more sets of weights are available, it is more efficient to use single weights from one set as the closure weights for another. The weights so employed are called CHECK WEIGHTS if the set being calibrated is new or has been submitted from outside the laboratory.

Check weights are calibrated along with a decade and, as their name implies, provide a check on the calibration procedure. The philosophy of usage is that if a laboratory is unable to calibrate one of its own well-known weights, then something is seriously wrong with the calibration [12]. In addition, the check weights are also the reference weights used for calibration of the next lower decades of their sets. Each time a check weight is used, a new datum is added to the pool from which the cumulative mean of its correction is derived. This increases its value as a reference weight.

Sets Submitted for Calibration

Consider a complete set of weights submitted for calibration whose members' corrections are entirely unknown. Calibration may be carried out ab initio using the methods of this report. Alternatively it may be done with a much higher degree of confidence with the aid of a reference set of weights whose members' cumulative mean corrections and variances are well documented.

In the latter case, the reference weight and a check weight are drawn from the reference set for the calibration of each unknown decade, say the first.

The reference weight for the second decade is the check weight used for the first, and a new check weight is drawn from the reference set. This procedure is simply repeated for the entire unknown set.

The sensitivity weights may be drawn from the reference set, in which case check weight verification may be carried out decade by decade. If they are drawn from the unknown set, then verification must follow recalibration of the set following the procedures of Section D. There does not seem to be any obvious advantage to following this more lengthy method.

In conclusion, it may be remarked that the methods outlined here may be used to advantage in any mass calibration program, regardless of target accuracy.

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Appendix A: The Pound Avoirdupois System

For historical and legal reasons, mass laboratories are required to calibrate sets of weights based on the pound as a reference mass. For this reason, there exists a requirement for orthogonal design matrices for calibration in the pound avoirdupois system.

The pound is defined as follows [9].

$$1\ \text{lb} = 0.453\ 592\ 37\ \text{kg} \tag{1}$$

and is divided into 16 ounces (oz) and each ounce is divided into 16 drams (dr). Weight sets in the pound system lend themselves to organization in binary series.

Binary Series 8, 4, 2, 1, 1'

We define a BINARY SERIES as a set of weights arranged in powers of two with the smallest nominal mass duplicated, as in this example. Here the series might be in ounce units to be calibrated in terms of a reference pound (16 ounces) or in dram units to be calibrated using a reference ounce (16 drams).

Since in any binary series a given mass may be compared only with the sum of all smaller masses in the series, the orthogonal design matrix is both unique and easy to construct.

The design matrix and deflection vector for all possible combinations of weights is given by

$$\begin{array}{c} 8\ \ 4\ \ 2\ \ 1\ \ 1' \\ \begin{vmatrix} 1 & 1 & 1 & 1 & 1 \\ 1 & -1 & -1 & -1 & -1 \\ 0 & 1 & -1 & -1 & -1 \\ 0 & 0 & 1 & -1 & -1 \\ 0 & 0 & 0 & 1 & -1 \end{vmatrix} \end{array} \qquad \begin{vmatrix} c_8 \\ c_4 \\ c_2 \\ c_1 \\ c_1' \end{vmatrix} = \begin{vmatrix} d_1 + c_{16} \\ d_2 \\ d_3 \\ d_4 \\ d_5 \end{vmatrix} \tag{2}$$

No redundancies exist and (A10) produces only four distinct equations for the frequencies of usage:

$$
\begin{aligned}
0 &= f_1 - f_2 \\
0 &= f_1 + f_2 - f_3 \\
0 &= f_1 + f_2 + f_3 - f_4 \\
0 &= f_1 + f_2 + f_3 - f_5
\end{aligned}
\tag{3}
$$

with the solutions

$$
\begin{aligned}
f_1 &= f_2 = 1 \\
f_3 &= 2 \\
f_4 &= 4 \\
f_5 &= 8
\end{aligned}
\tag{4}
$$

Total Operations = 16

The new orthogonal design matrix and deflection vector are given by

$$
\begin{array}{c}
\begin{array}{ccccc} 8 & 4 & 2 & 1 & 1' \end{array} \\
\left|\begin{array}{ccccc}
1 & 1 & 1 & 1 & 1 \\
1 & -1 & -1 & -1 & -1 \\
0 & 1 & -1 & -1 & -1 \\
0 & 1 & -1 & -1 & -1 \\
0 & 0 & 1 & -1 & -1 \\
\hline
0 & 0 & 1 & -1 & -1 \\
0 & 0 & 0 & 1 & -1 \\
\hline
0 & 0 & 0 & 1 & -1
\end{array}\right|
\end{array}
\qquad
\left|\begin{array}{c} c_8 \\ c_4 \\ c_2 \\ c_1 \\ c_1' \end{array}\right| = \left|\begin{array}{l}
d_1 + c_{16} \\
d_2 \\
(d_3)' \\
\dfrac{d_4}{(d_4)'''} \\
\dfrac{d_5}{(d_5)'''''''}
\end{array}\right|.
\tag{5}
$$

From (5),

$$
T^{-1} = \left|\begin{array}{ccccc}
\frac{1}{2} & 0 & 0 & 0 & 0 \\
0 & \frac{1}{2} & 0 & 0 & 0 \\
0 & 0 & \frac{1}{8} & 0 & 0 \\
0 & 0 & 0 & \frac{1}{16} & 0 \\
0 & 0 & 0 & 0 & \frac{1}{16}
\end{array}\right|
\tag{6}
$$

and

$$A^T D = \begin{vmatrix} c_{16} + d_1 + d_2 \\ c_{16} + d_1 - d_2 + \sum^{2} d_3 \\ c_{16} + d_1 - d_2 - \sum^{2} d_3 + \sum^{4} d_4 \\ c_{16} + d_1 - d_2 - \sum^{2} d_3 - \sum^{4} d_4 + \sum^{8} d_5 \\ c_{16} + d_1 - d_2 - \sum^{2} d_3 - \sum^{2} d_4 - \sum^{8} d_5 \end{vmatrix} = \begin{vmatrix} c_{16} + S_8 \\ c_{16} + S_4 \\ c_{16} + S_2 \\ c_{16} + S_1 \\ c_{16} + S_1' \end{vmatrix} \tag{7}$$

Using (6) and (7) in (A9), the calibration equations are

$$\begin{aligned} c_8 &= \frac{1}{2}(c_{16} + S_8) \\ c_4 &= \frac{1}{4}(c_{16} + S_4) \\ c_2 &= \frac{1}{8}(c_{16} + S_2) \\ c_1 &= \frac{1}{16}(c_{16} + S_1) \\ c_1' &= \frac{1}{16}(c_{16} + S_1') \end{aligned} \tag{8}$$

The general form of (8) is

$$c_n = \frac{n}{16}(c_{16} + S_n) \tag{9}$$

Series 8, 4, 2, 1, ½, ¼

This is a common series used in the pound system, where the reference weight is 16 ounces or drams. It may appear to be a long form of the series previously discussed. However it is actually a binary series as already defined, with six instead of five members. The entire series is just multiplied by 2.

The progression of values exhibited by all of the equations so far developed in this appendix make further detailed comment on this series redundant.